



TITLE:

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(INTERFACE SCIENCE-Separation Chemistry)

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# Molecular Design of Chelating Ligands with Highly Selective Recognition and Separation Functions for Group 13 Metal Ions

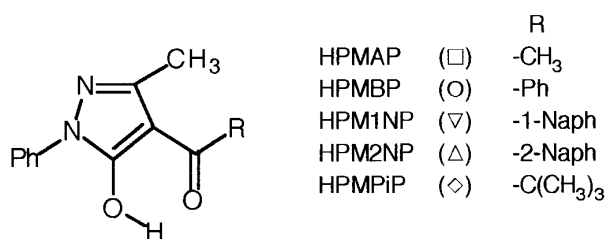
Shigeo Umetani, Quyen T. H. Le and Masakazu Matsui

Highly selective ligands for group 13 metal ions ( $\text{Al}^{3+}$ ,  $\text{Ga}^{3+}$  and  $\text{In}^{3+}$ ) have been successfully designed taking into consideration the bite size (O-O distance in the chelate ring) and the interligand contact in the complex. The complexation of  $\text{Al}^{3+}$  was found to be under the effect of the interligand contact and that of  $\text{In}^{3+}$  the bite size. The appropriate substituents were introduced to  $\beta$ -diketone type ligands to control the bite size and the volume of the ligand.

**Keywords:** Solvent extraction /  $\beta$ -Diketone / Acylpyrazolone / Molecular recognition / Substituent effect / Bite size / Interligand contact

Studies on the solvent extraction with modified  $\beta$ -diketones such as  $\alpha$ -phenylacetylacetone (PhAA) or  $\alpha$ -phenylbenzoylacetone (PhBA) revealed that the complexations of group 13 metal ions are strongly affected by the bite size (O-O distance in the chelate ring) and the interligand contact in the complex [1].  $\text{Al}^{3+}$  and  $\text{In}^{3+}$  are readily extracted into the benzene phase with AA and BA in the order,  $\text{Al}^{3+} > \text{In}^{3+}$ . On the other hand,  $\text{In}^{3+}$  was totally unextractable with PhAA and PhBA. Considering that the phenyl group is introduced at the  $\alpha$ -position, which is the opposite side of the complexation site, those extraction behaviors are surprising. The X-ray crystallographic studies on the structures of In  $\beta$ -diketonates show that the bite size in the In complex is one of the longest among the metal  $\beta$ -diketonates and the complexation of  $\text{In}^{3+}$  is disturbed by the substituent at the  $\alpha$ -position of  $\beta$ -diketone, which prevents the O-O distance from widening to fit the

structure of the complex. In addition, the complexation of  $\text{Al}^{3+}$  was found to be under the great influence of the interligand contact due to its remarkably small ionic radius.  $\text{Al}^{3+}$  is usually extracted better than  $\text{In}^{3+}$  owing to the smaller ionic radius, however, the opposite extraction order is seen for the extractants having bulk terminal substituents such as



## INTERFACE SCIENCE —Separation Chemistry—

### Scope of research

*Our research activities are concerned in selective complex formation systems (molecular recognition). Major subjects of the research are followings: (1) Design and synthesis of the selective complex formation systems. Ligands (host molecules) that have novel functions in separation of metal ions and guest molecules are designed and synthesized. Their functions are analyzed basing on structures of the ligands and complexes. (2) Biogeochemistry of trace elements in the hydrosphere. Novel analytical methods for trace elements are developed. The behavior of trace elements in the hydrosphere is explored.*



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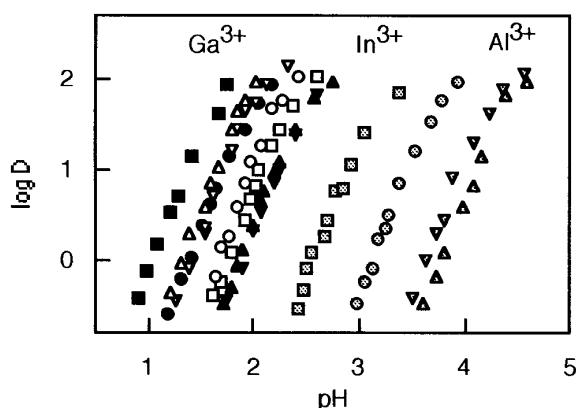
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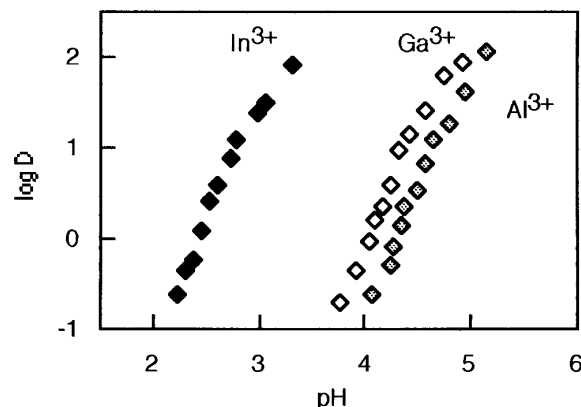
dibenzoylmethane and thenoyltrifluoroacetone. Thus, the extraction of  $\text{Al}^{3+}$  is expected to be lowered by the bulky terminal substituents. Highly selective ligands for group 13 metals ( $\text{Al}^{3+}$ ,  $\text{Ga}^{3+}$ ,  $\text{In}^{3+}$ ) have been successfully designed taking the two factors into consideration.

Five acylpyrazolone derivatives have been prepared as seen in the scheme. They are 1-phenyl-3-methyl-4-acetyl (HPMAP), -benzoyl (HPMBP), -(1-naphthoyl) (HPM1NP), -(2-naphthoyl) (HPM2NP), and -pivaloyl (HPMPiP) -pyrazolones. The O-O distances were estimated by the MNDO/H calculation, which is MNDO that takes into consideration the hydrogen bonding and has been found to be most suitable among the semi-empirical molecular orbital calculations to evaluate the structures of  $\beta$ -diketone type organic ligands [2]. The O-O distances of the acylpyrazolones except for HPMPiP are 2.60 - 2.65 Å, while that of HPMPiP is 2.46 Å. The  $^1\text{H}$ -NMR spectra show the evidence for the hydrogen bond strength. The signal assigned to the hydroxyl proton of HPMPiP appeared at  $\delta$  14.9; whereas those for the other acylpyrazolones are too broad to observe at  $\delta$  10-20. This signal did not move through changing the concentration (0.01 - 0.1 mol dm $^{-3}$ ) and was found to disappear after adding D $_2$ O. It was reported that the hydrogen bonded enolic proton signal appears at that low magnetic field.



**Figure 1** Extraction of  $\text{Al}^{3+}$  (gray symbols),  $\text{Ga}^{3+}$  (solid symbols) and  $\text{In}^{3+}$  (blank symbols) into benzene with acylpyrazolones. [acylpyrazolone] $_0$  =  $5 \times 10^{-3}$  mol dm $^{-3}$  in benzene.  $[\text{NaClO}_4]$  = 0.1 mol dm $^{-3}$ .

The extractions of  $\text{Al}^{3+}$ ,  $\text{In}^{3+}$  and  $\text{Ga}^{3+}$  into benzene are shown in Fig.1 plotting the logarithmic value of the distribution ratio of metal ions (D) against pH. Being derived from the five membered heterocyclic 4-pyrazolone, the O-O distances of the present acylpyrazolone derivatives except for HPMPiP are longer than those of the conventional  $\beta$ -diketones. Owing to their long O-O distances, the extraction of  $\text{In}^{3+}$  was not disturbed and was made at pH 1-2. The extraction of  $\text{Al}^{3+}$  was seen in the higher pH region, although



**Figure 2** Extraction with HPMPiP.  $[\text{HPMPiP}]_0$  =  $5 \times 10^{-3}$  mol dm $^{-3}$  in benzene.  $[\text{NaClO}_4]$  = 0.1 mol dm $^{-3}$ .

the ionic radius of  $\text{Al}^{3+}$  is much smaller than that of  $\text{In}^{3+}$ . Considering that the acylpyrazolones themselves are bulky ligands and their acidities are quite similar, it is clear that the extraction of  $\text{Al}^{3+}$  is under the effect of the interligand contact. It was found that the extraction reduces as the substituent at the 4-position becomes bulkier. The quantitative separation of  $\text{Al}^{3+}$  from  $\text{In}^{3+}$  can be readily achieved with the naphthoylpyrazolones. The extraction of  $\text{In}^{3+}$  does not depend on the size of the substituents. The effect of the interligand contact is also seen in the extraction of  $\text{Ga}^{3+}$ . While the ionic radius of  $\text{Ga}^{3+}$  is smaller than that of  $\text{In}^{3+}$ , their extractions were similar. In addition, the extractability decreases as the substituents become bulkier like the case of  $\text{Al}^{3+}$ . All of the acylpyrazolones examined are available to quantitatively separate  $\text{Al}^{3+}$  and  $\text{Ga}^{3+}$ . Owing to the steric repulsion between the 4-pivaloyl and 3-methyl groups, the O-O distance of HPMPiP is narrowed and the extraction of  $\text{In}^{3+}$  came close to that of  $\text{Al}^{3+}$  as seen in Fig. 2, resulting in a quantitative separation of  $\text{Ga}^{3+}$  from  $\text{Al}^{3+}$  and  $\text{In}^{3+}$ .

From our results so far, there are two factors governing the complexation of group 13 metal ions with  $\beta$ -diketones: the distance between the two donating oxygens and the interligand interaction, and their balance should decide the stability of each complex, that is, the extraction order, as well as the separation of  $\text{Al}^{3+}$  and  $\text{In}^{3+}$ . This observation may contribute to the basic knowledge on organic ligands, especially on the concepts of their complexation with metal ions, and confirms our suggestion for a perspective strategy for designing novel ligands of high selectivity from well-known typical ones [2].

## References

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2. Le T H Q, Umetani S, Suzuki M, Matsui M, *J. Chem. Soc., Dalton Trans.*, in press.